Photoinduced Optical Rotation in a Racemic Mixture of Hydrogen Peroxide Molecules

B. A. Grishanin and V. N. Zadkov
International Laser Center and Faculty of Physics
M. V. Lomonosov Moscow State University, Moscow 119899, Russia

A problem of inducing a required sign of chirality in a racemic mixture of enantiomers of a chiral molecule is analyzed. As an example, a racemic mixture (vapor) of left- and right-handed enantiomers of hydrogen peroxide (H_2O_2) molecule is considered. It is shown that biharmonic Raman excitation of the splitted due to the left-right conversion internal rotation levels can be effectively used for inducing optical activity in the initially racemic vapor of H_2O_2 molecules. An experiment to study this photoinduced optical rotation is discussed.

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I. INTRODUCTION

Chiral specificity of the bioorganic world is one of the most intriguing phenomenon of Nature [1–4]. It is often thought to reflect mirror breaking responsible for a life with a given 'sign of chirality', in the absence of any evidence of 'mirror-antipode' life [5–8]. Physical origins of this symmetry breaking are not completely understood yet. Along with spontaneous symmetry breaking studies, understanding that optical methods, specifically methods of nonlinear optics [9], could be used not just to monitor, but also to control chiral symmetry of molecules seems to be of great importance.

In this paper we investigate a possibility of excitation of the chiral-asymmetric states of the hydrogen peroxide molecule (H_2O_2) driven by a laser pulse parameters of which (duration and laser field intensity) fit special requirements discussed in the paper. Hydrogen peroxide molecule (Fig. 1a) is a simplest chiral molecule geometry of which is non-invariant with respect to the coordinate inversion transformation $(X, Y, Z) \to (X, Y, -Z)$.

When this transformation is applied the mirror-image of the molecule cannot be mapped with the original with the help of any rotation transformation because the torsional angles of the molecule $\pm\theta = \pm(\theta_1 - \theta_2)$ are not equivalent. When we select between left- or right-handed frame, a choice of the direction of the vector $\mathbf{n}_{\mathrm{O}}$ from one atom to another allows us then to assign a definite sign to the torsional angle $\angle$HOOH. An equilibrium value of the torsional angle in the gas phase in accordance with theoretical calculations and experimental data is $\theta \simeq \pm 120^\circ$ [10–13], where positive sign corresponds to the shown in Fig. 1a so-called d-state (right-handed enantiomer) and negative—to the l-state (left-handed enantiomer).

A rough understanding of the effect of photoinduced switching between left- and right-handed enantiomers of H_2O_2 molecule may be obtained as follows. This molecule has a characteristic double well torsional potential shape. Existence of the mirror symmetry of the minima of the torsional potential leads to the splitting of energy states as a result of tunneling through the lower barrier. The resulting eigen states being presented with the even and odd wave functions ψ_S, ψ_A (tunneling through the higher barrier and the corresponding additional splitting are negligible [13]). Relatively large splitting value $\Delta E_0 = 11.4\ \mathrm{cm}^{-1}$ corresponds to the absence of stationary chiral-asymmetric states, which actually oscillate with the frequency $\omega_0 = E_0/\hbar$ between the stationary states ψ_S, ψ_A until the symmetric equilibrium is reached. As a result, one can manipulate the chiral properties of H_2O_2 molecule inducing tunneling between d- and l-enantiomers and therefore the effect of photoinduced optical rotation has an oscillating character. By contrast, for the case of heavier molecules tunneling time between different enantiomers of which may be infinitely large and initially produced chiral asymmetric state is stable.

The Hamiltonian of molecule–laser field interaction $\hat{H}_I = -\sum \mathbf{d}_k \mathbf{E}(\mathbf{r}_k)$ displays a qualitative difference in dipole (H_D) and quadrupole (H_Q) approximations. In dipole approximation (at $\mathbf{E}(\mathbf{r}_k) \to \mathbf{E}(\mathbf{r}_0)$) proton contributions are added, whereas in quadrupole approximation (at $\mathbf{E}(\mathbf{r}_k) \to (\mathbf{r}_k - \mathbf{r}_0)\nabla\,\mathbf{E}(\mathbf{r}_0)$) they are substracted. As a result, H_D is an even function of the torsional angle and H_Q is an odd one. For the corresponding off-diagonal matrix elements H_D^{12}, H_Q^{12} of the $S \to A$ transition we get

$$H_D^{12} = 0, \quad H_Q^{12} \neq 0. \tag{1}$$

This means that the precession between the tunneling splitted right and left chiral states ($d \leftrightarrow l$) can be excited only due to the quadrupole interaction, whereas the dipole interaction causes only modulation of the eigen states energies,

oscillating with the frequency of the exciting laser field. In other words, we can *selectively* excite due to the quadrupole interaction *d*- or *l*-enantiomers using one of the most fundamental quantum optics effects—coherent precession of a two-level system under the action of a coherent pulse of electromagnetic field.

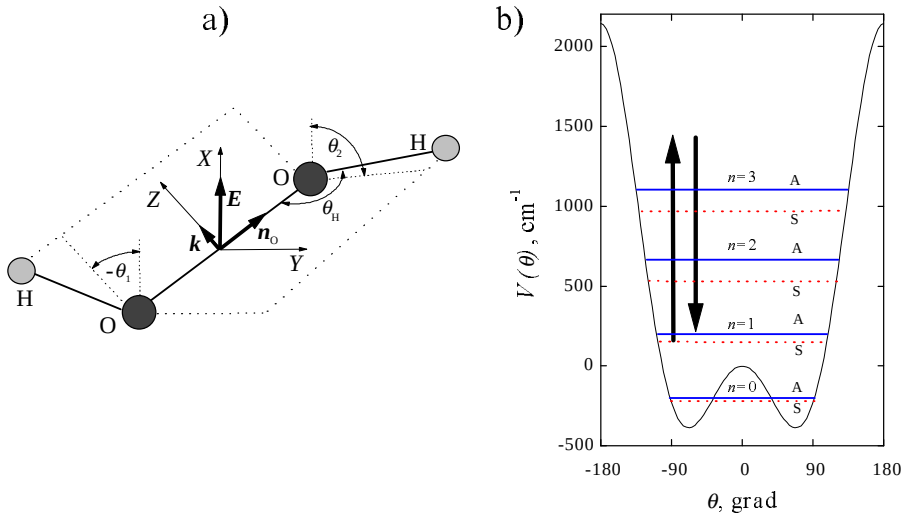

FIG. 1. a) Geometry of H_2O_2 molecule in *d*-configuration interacting with the incident laser field **E** wave vector **k** of which is directed along the Z axis. Equilibrium valence angles for hydrogen atoms are equal to $\theta_H \approx 100°$, $a_O \approx 1.461$ Å and $a_H = 0.964$ Å are the O–O and O–H bond lengths, correspondingly, $\mathbf{n}_O$ is the direction vector of the O–O bond, θ_1, θ_2 are the internal rotation angles ($\theta = \theta_1 - \theta_2$ is the torsional angle). b) Model torsional potential function $V(\theta)$. Pictured lower vibrational levels are splitted due to the tunneling through the isomerization barrier into symmetric (dotted line) and antisymmetric (solid line) states.

In this paper we discuss the conditions under which the effect of photo-induced chirality can be studied experimentally by registering the corresponding photoinduced optical activity in a racemic mixture of left- and right-handed enantiomers of the H_2O_2 molecule, which shows no optical activity otherwise.

A rough estimate of the order of magnitude of the discussed effect can be made within the model of one-photon excitation. The criterion of alignment of the molecules dipole moments along Z axis for 100% of the molecules in a solution under the action of dc electric field with the magnitude E can be written as $Eea_H \gg kT$ (a_H is the O–H bond length, e is the proton charge), which at the room temperature gives $E \gg 10^6$ V/cm. If we do not require that 100% of the molecules in the solution are to be aligned, we can then use relatively moderate field intensities and therefore achieve a smaller degree of alignment $\varkappa = Eea_H/kT$, which however may be enough to determine experimentally optical activity in the initially racemic solution.

In the frequency region of electronic susceptibility, the effect can be estimated to the lowest order under the suggestion that $\varkappa$ represents the part of molecules aligned strictly along the field, whereas the rest of the molecules do not contribute to the effect. Then the upper estimate can be obtained by multiplying the typical specific rotation value $\alpha \sim 10^2$ deg·cm^3/g·dm for the media with strong optical activity by the small parameter $\varkappa$, which gives us finally $\sim 10^{-1}$ deg·cm^3/g·dm for the resonantly excited optical activity at $E \approx 10^3$ V/cm. For a vapor at normal conditions and at the interaction length of 1 dm the rotation angle is about $0.1''$. This value is about the sensitivity limit of the linear polarization spectroscopy methods. Therefore, even without going into other obstacles, it seems difficult to observe the effect of photoinduced optical rotation in the scheme with one-photon resonant excitation and using dc electric field for aligning the molecules.

Additional trouble is the finite lifetime τ_r of the chiral state due to the molecular collisions in a solution. This time should be at least longer than the time the laser field travels through the active region $\tau_c = L/c \geq 10^{-10}$ s^{-1} and its lower bound estimate is given by $\tau_r = (\mathcal{N}v\sigma)^{-1}$, where $\mathcal{N}$ is the molecular concentration, v is the heat velocity and σ is the collisional cross section. At the normal conditions one gets $\tau_r \sim 10^{-9}$ s$^{-1} > \tau_c$.

Two-photon Raman excitation scheme we discuss in this paper fits the above condition and, beyond that, provides an effective excitation of the required chiral state of the molecule using lasers in the convenient frequency range.

II. H_2O_2 MOLECULE'S DYNAMICS IN ELECTROMAGNETIC FIELD

A. Reduced model of free molecule's dynamics

To describe free molecule's dynamics driven by the laser field we shall start with the mathematical description of free molecule's dynamics. For this it seems helpful to reduce the total molecular Hamiltonian using the fact that proton to oxygen mass ratio is a small one. Then the protons' dynamics can be treated adiabatically with respect to the oxygen coordinates so that the dynamics of oxygen nuclei can be calculated by averaging over direction of the unit vector $\mathbf{n}_{\rm O} = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta)$ along the O–O bond. Averaging along Z-coordinate (Fig. 1a) should be performed then only for protons rotation about the O–O bond, which potential depends only on the torsion angle $\theta = \theta_2 - \theta_1$.

Under these conditions, the molecular Hamiltonian in a reduced model, which includes both the free molecule's rotation about the O–O bond and torsional oscillations, takes the form:

$$\hat{H} = \hat{H}_{\rm H} + \hat{H}_\theta \tag{2}$$

with

$$\hat{H}_{\rm H} = -\frac{\hbar^2}{4m_{\rm H}r_{\rm H}^2}\frac{\partial^2}{\partial\tilde{\theta}^2}, \tag{3}$$

$$\hat{H}_\theta = -\frac{\hbar^2}{m_{\rm H}r_{\rm H}^2}\frac{\partial^2}{\partial\theta^2} + V(\theta), \tag{4}$$

where $\tilde{\theta} = (\theta_1 + \theta_2)/2$, $m_{\rm H}$ is the proton mass and $V(\theta)$ is the torsional potential. For simplicity, we neglect the vibrations of the valence angles $\angle$HOO.

Initial molecule's position, which can be referred to as the mean angle $\tilde{\theta}$, includes, in addition to the above mentioned uncertainty in direction $\mathbf{n}_{\rm O}$, an uncertainty due to the molecule's rotation about this direction, which corresponds to the third rotational degree of freedom plus to the two angles that determine the direction of $\mathbf{n}_{\rm O}$. Corresponding to the free rotation about O–O bond transition frequencies $\omega_{n\to n+1} = 7.84 \times (n + 1/2)$ cm^{-1} calculated from (3), (4) are four times smaller than the corresponding frequencies of internal rotation, which are determined by the torsional potential $V(\theta)$.

B. Photoexcitation of molecule's rotational degrees of freedom

In this section we will discuss a model of molecule–laser field interaction with an accent placed on the photoexcitation of molecule's rotational degrees of freedom. Let us consider H_2O_2 molecule interacting with the laser field $\mathbf{E}(t) = \mathbf{E}_1 u_1(t)\cos(\omega_1 t + \varphi_1)$ with the pulse envelope $u_1(t)$ and frequency $\omega_1 \gg \omega_{n\to n+1}$, so that we can neglect the quantum specificity of the excitation. The following classical equation governs then the rotational dynamics of the molecule:

$$J\frac{d^2\tilde{\theta}}{dt^2} = \frac{\partial}{\partial\tilde{\theta}}\mathbf{E}(t)\mathbf{d},$$

where J is the molecule's moment of inertia.

In zero'th order with respect to the angle deviation for the acting force in the right side of the equation and in the case of not too short laser pulses ($\tau_1 \gg 1/\omega_1$) the angle response $\Delta\tilde{\theta}$ at the frequency ω_1 takes the form:

$$\Delta\tilde{\theta}(\omega_1) \simeq -\frac{\partial}{\partial\tilde{\theta}}\frac{\mathbf{E}_1(t)\mathbf{d}}{J\omega_1^2}. \tag{5}$$

This angle deviation causes the modulation of the quadrupole Hamiltonian at the frequency ω_1, which in its turn causes the internal rotation of the molecule and therefore leads to the partial aligning of the molecule. The latter reveals in modification of the quadrupole Hamiltonian rotational symmetry. In particular, in case the O–O bond directs along Z axis, i.e. $\vartheta = 0$, and the laser field $\mathbf{E}_1$ shines along Y axis, the rotational symmetry leads to a homogeneous distribution versus angle $\tilde{\theta}$, dependence on which in the quadrupole moment is given by $\sin\tilde{\theta}$. Molecule's orientation reveals then in the angle response, which can be extracted from Eq. (5) in the form

$$\Delta\tilde{\theta} \simeq \frac{E_1 d}{2J\omega_1^2}u_1(t)\cos\tilde{\theta}\cos\frac{\theta}{2}\cos(\omega_1 t + \varphi_1), \tag{6}$$

where the angle dependence $\cos\tilde{\theta}$ follows that one of the quadrupole Hamiltonian for the laser field $\mathbf{E}_2 \| X$, so that

$$\Delta\hat{H}_Q = \partial\hat{H}_Q/\partial\tilde{\theta}\,\Delta\tilde{\theta} \propto \cos^2\tilde{\theta}.$$

Estimation of the order of magnitude for the visual range of optical frequencies is given by

$$\Delta\tilde{\theta} \sim 10^{-10}\sqrt{I_1}, \tag{7}$$

where I_1 is the $\mathbf{E}_1$ field intensity in W/cm^2 and the angle is given in radians. This estimate goes to 1 only for the field strengths larger than atomic ones.

Torsional oscillations dynamics describing by the Hamiltonian $\hat{H}_\theta$ is essentially quantum one due to the relatively small proton to oxygen mass ratio. This leads to the tunneling between the d and l local minima of the torsional potential (Fig. 1b) and therefore to two energy-splitted superposition eigen states ψ_S, ψ_A with equally represented d- and l-configurations. In addition, it determines the non-rigidity of molecule's geometry due to the quantum uncertainty of the wave functions versus torsional angle. Torsional potential of H_2O_2 molecule and its eigen energies have been extensively explored by *ab initio* calculations and respective fitting to the experimental spectra. The torsional potential and corresponding energy levels structure taken for our calculations from [13] are shown in Fig. 1b. With this potential, an estimate for the local states uncertainty on torsional angle, which is based on expression for the fluctuations in vacuum state of a harmonic oscillator, gives $\sigma_\theta \approx [\hbar/(m_H r_H^2 \omega_0)]^{1/2} \approx 20^\circ$.

The interaction Hamiltonian in dipole approximation, which takes into account only proton charges displacements, has the form:

$$\hat{H}_D = -E_L e a_\mathrm{H} \Re\mathbf{e}(\mathbf{e}_1 + \mathbf{e}_2), \tag{8}$$

where $\mathbf{e}_{1,2}$ are the corresponding unit direction vectors of the protons bonds, $\mathbf{e}$ is the laser field polarization vector and e is the proton charge. The quadrupole contribution to the interaction Hamiltonian depends on the choice of the center of frame. Its displacement causes an additional contribution to the dipole Hamiltonian, which is however small and can be neglected as it displays the same qualitative interaction properties as the main term. In our calculations we therefore choose the center of frame as it is shown in Fig. 1a in order to simplify the Hamiltonian. The corresponding expression takes the form:

$$\hat{H}_Q = -\mathbf{E}_L\mathbf{d}_Q = -\frac{\mathbf{k}\mathbf{n}_\mathrm{O} a_\mathrm{O}}{2} E_L e a_\mathrm{H} \Re e\, i\mathbf{e}(\mathbf{e}_2 - \mathbf{e}_1), \tag{9}$$

where a_O is the O–O bond length. The discussed choice of the center of frame leads to the dependence of quadrupole Hamiltonian H_Q on torsional angle given by the odd function $\sin\theta/2$.

To proceed with calculations of Eqs (8), (9) the polarization vector should be represented in the form $\mathbf{e} = (e_X, e_Y, 0)$ with the components e_X, e_Y, which are generally the complex numbers. Then the corresponding coefficients

$$C_{H_k} = \mathbf{n}_X \cdot \mathbf{n}_{H_k}, \qquad S_{H_k} = \mathbf{n}_Y \cdot \mathbf{n}_{H_k}$$

can be calculated analytically. Here $\mathbf{n}_X$, $\mathbf{n}_Y$ are the unit vectors along axes X, Y and $\mathbf{n}_{H_k}$ are the unit vectors along the bonds O–H$_k$, $k = 1, 2$. Under these notations Hamiltonians (8), (9) take the form

$$\begin{aligned} \hat{H}_D &= -E_L e a_\mathrm{H} \Re e\, e^{-i\varphi_L}[e_X(C_{H_1} + C_{H_2}) + e_Y(S_{H_1} + S_{H_2})], \\ \hat{H}_Q &= -\frac{k_L a_\mathrm{O}}{2} E_L e a_\mathrm{H} \Re e\, i e^{-i\varphi_L}[e_X(C_{H_2} - C_{H_1}) + e_Y(S_{H_2} - S_{H_1})], \end{aligned} \tag{10}$$

where k_L is the modulus of the laser field wave vector, φ_L is the laser field phase, and rotation angles $\theta_{1,2}$ of proton bonds represent coordinate operators. The projection coefficients of the proton dipole moments onto the directions X, Y of the polarization vector $\mathbf{e}$ are given by the following formulae

$$\begin{aligned} C_{H_k} &= \mathbf{n}_X\, O(\mathbf{n}^\perp_{OOH_1}, \delta_H) O(\mathbf{n}_\mathrm{O}, \theta_k)\, O(\mathbf{n}^\perp_{\mathbf{n}_X\mathbf{n}_O}, \pi/2 - \angle\,\mathbf{n}_X\mathbf{n}_\mathrm{O})\, \mathbf{n}_X, \\ S_{H_k} &= \mathbf{n}_Y\, O(\mathbf{n}^\perp_{OOH_2}, \delta_H) O(\mathbf{n}_\mathrm{O}, \theta_k)\, O(\mathbf{n}^\perp_{\mathbf{n}_X\mathbf{n}_O}, \pi/2 - \angle\,\mathbf{n}_X\mathbf{n}_\mathrm{O})\, \mathbf{n}_X \end{aligned}$$

as the scalar product of vector $\mathbf{n}_{X,Y}$ and another vector obtained as follows. First, the vector $\mathbf{n}_X$ is rotated at the angle $\pi/2 - \angle\,\mathbf{n}_X\mathbf{n}_\mathrm{O}$ in the plain $\mathbf{n}_X\mathbf{n}_\mathrm{O}$ until it is perpendicular to the axis $\mathbf{n}_\mathrm{O}$ which is used as a reference axis torsional angles are calculated in respect to which. Second, the vector $\mathbf{n}_X$ is rotated about axis O—O at the torsional angle θ_k. Third, the subsequent rotation of $\mathbf{n}_X$ vector is performed in the plane OOH$_k$ at the angle $\delta_H = \theta_H - \pi/2$ until we get the unit vector along the vector $\mathbf{n}_{\mathrm{H_k}}$.

When non-zero value δ_H is taken into account, analytical expressions for the above listed coefficients derived with the use of computer algebra are bulky, so that we list them here for a specific case of $\delta_H = 0$, i.e., for the case when the proton bonds are orthogonal to the bond O–O. The corresponding error is then not larger than $\sim 10\%$ due to the small value of $\delta_H \approx 10^\circ$. The matrix of three-dimensional rotations at angle α about axis $\mathbf{n}$ is given then by

$$O(\mathbf{n},\alpha)=\begin{pmatrix} n_x^2+n_y^2\cos\alpha+n_z^2\cos\alpha & n_xn_y-n_xn_y\cos\alpha-n_z\sin\alpha & n_xn_z-n_xn_z\cos\alpha+n_y\sin\alpha \\ n_xn_y-n_xn_y\cos\alpha+n_z\sin\alpha & n_y^2+n_x^2\cos\alpha+n_z^2\cos\alpha & n_yn_z-n_yn_z\cos\alpha-n_x\sin\alpha \\ n_xn_z-n_xn_z\cos\alpha-n_y\sin\alpha & n_yn_z-n_yn_z\cos\alpha+n_x\sin\alpha & n_z^2+n_x^2\cos\alpha+n_y^2\cos\alpha \end{pmatrix}.$$

With the use of this expression the resulting coefficients takes the form:

$$\begin{aligned} & C_{H_1}=\sqrt{1\sin^2\vartheta\cos^2\varphi}\cos\theta_1\,, \quad C_{H_2}=\sqrt{1-\sin^2\vartheta\cos^2\varphi}\cos\theta_2\,, \\ S_{H_1} &= \left(16\sqrt{\cos^2\vartheta+\sin^2\varphi\sin^2\vartheta}\right)^{-1}[-2\sin(2\varphi-\theta_1)+\sin(2\varphi-2\vartheta-\theta_1)-8\sin(\vartheta-\theta_1)+ \\ & +\sin(2\varphi+2\vartheta-\theta_1)-2\sin(2\varphi+\theta_1)+\sin(2\varphi-2\vartheta+\theta_1)+8\sin(\vartheta+\theta_1)+\sin(2\varphi+2\vartheta+\theta_1)]\,, \\ S_{H_2} &= \left(16\sqrt{\cos^2\vartheta+\sin^2\varphi\sin^2\vartheta}\right)^{-1}[-2\sin(2\varphi-\theta_2)+\sin(2\varphi-2\vartheta-\theta_2)-8\sin(\vartheta-\theta_2)+ \\ & +\sin(2\varphi+2\vartheta-\theta_2)-2\sin(2\varphi+\theta_2)+\sin(2\varphi-2\vartheta+\theta_2)+8\sin(\vartheta+\theta_2)+\sin(2\varphi+2\vartheta+\theta_2)]\,. \end{aligned} \tag{11}$$

For the sum of the coefficients determining the dipole interaction potential we get then the following expressions

$$\begin{aligned} & C_{H_1}+C_{H_2}=C_+\cos\frac{\theta}{2}\,, \quad S_{H_1}+S_{H_2}=S_+\cos\frac{\theta}{2}\,, \quad C_+=2\sqrt{1-\sin^2\vartheta\cos^2\varphi}\,\cos\tilde\theta\,, \\ S_+ &= 2\left(16\sqrt{\cos^2\vartheta+2\sin^2\varphi\sin^2\vartheta}\right)^{-1}[-2\sin(2\varphi-\tilde\theta)-2\sin(2\varphi+\tilde\theta)+\sin(2\varphi-\tilde\theta-2\vartheta)+ \\ & +\sin(2\varphi+\tilde\theta-2\vartheta)+8\sin(\tilde\theta-\vartheta)+8\sin(\tilde\theta+\vartheta)+\sin(2\varphi-\tilde\theta+2\vartheta)+\sin(2\varphi+\tilde\theta+2\vartheta)], \end{aligned} \tag{12}$$

which depend on the torsional angle as the even function $\cos\theta/2$. For the difference of the coefficients determining quadrupole interaction potential we get the following expressions, which depend on the torsional angle as the odd function $\sin\theta/2$:

$$\begin{aligned} & C_{H_2}-C_{H_1}=C_-\sin\frac{\theta}{2}\,, \qquad S_{H_2}-S_{H_1}=S_-\sin\frac{\theta}{2}\,, \quad C_-=-2\sqrt{1-\sin^2\vartheta\cos^2\varphi}\,\sin\tilde\theta\,, \\ S_- &= \left(16\sqrt{\cos^2\vartheta+2\sin^2\varphi\sin^2\vartheta}\right)^{-1}[(2\cos(2\varphi-\tilde\theta)-2\cos(2\varphi+\tilde\theta)-\cos(2\varphi-\tilde\theta-2\vartheta)+ \\ & +\cos(2\varphi+\tilde\theta-2\vartheta)+8\cos(\tilde\theta-\vartheta)+8\cos(\tilde\theta+\vartheta)-\cos(2\varphi-\tilde\theta+2\vartheta)+\cos(2\varphi+\tilde\theta+2\vartheta)]. \end{aligned} \tag{13}$$

For the simplified analysis of both molecule's rotation about axis O–O and torsional oscillations, the numerical values of the torsional potential $V(\theta)$ are essential. The corresponding numbers for the energy splitting, which we adopted from [13], are as follows: $\Delta E_0 = 11.44$ cm^{-1}, $\Delta E_1 = 116.34$ cm^{-1}, $\Delta E_2 = 206.57$ cm^{-1}. For $n \geq 1$ they exceed the frequencies of free molecule rotation. Therefore, the transitions between the eigen states of the torsional Hamiltonian $\hat H_\theta$ can be described in terms of classical coordinate $\tilde\theta$.

III. PHOTOINDUCED INTERNAL ROTATION IN H_2O_2 MOLECULE

This section presents a discussion on photoinduced excitation of internal conversion in H_2O_2 between left- and right-handed enantiomers.

Torsional potential of H_2O_2 molecule has a characteristic double-well shape (Fig. 1b) minima of which correspond to the left- and right-handed enantiomers and are mirror-symmetrically spaced. As a result, the eigenstates of the torsional Hamiltonian split due to the tunneling through the potential energy barrier separating the two wells. It seems reasonable to assume that the splitting of the eigen states of the torsional Hamiltonian $\hat H_\theta$, or internal rotation frequencies, significantly exceed the rotation frequencies of a free molecule. Under this assumption, resonant laser excitation of the internal rotation transition causes negligibly small deviations in molecule's orientation angles ϑ, φ and a small deviation of the rotation angle $\tilde\theta$. Therefore, the symmetric, ψ_S, and antisymmetric, ψ_A, states of the torsional potential can be excited into a coherent superposition $C_A\psi_A + C_S\psi_S$. The transition energy between S- and A-states, ΔE_n, can be estimated as

$$\Delta E \sim \exp\left(-2\sqrt{m_{\rm H}a_{\rm H}^2\Delta V}\,\Delta\theta/\hbar\right),$$

where ΔV and $\Delta\theta$ are the characteristic values of the height and width of the potential barrier (Fig. 1b).

In case of resonant excitation with the frequency $\omega_0 = \Delta E_n/\hbar$ only resonant matrix elements in the Hamiltonians (10) remain essential and, therefore, torsional dynamics of the molecule can be essentially reduced to that one of the two-level system.

Let us now examine, for the case of linear polarization ($e_X = 1$, $e_Y = 0$)[1], the 2×2-matrix of the one-photon interaction Hamiltonian $\hat{H}_L$ of the total one-photon interaction Hamiltonian $\hat{H}_I = \hat{H}_D + \hat{H}_Q$, where with the help of Eqs (10) $\hat{H}_D \propto \cos\theta$ and $\hat{H}_Q \propto \sin\theta$. The total interaction Hamiltonian $\hat{H}_I$ can be written using Pauli matrices of the transition in the form:

$$\hat{H}_I \to V_{12}\hat{\sigma}^+ + V_{21}\hat{\sigma}^- = V_{12}(t)\hat{\sigma}_1(t) = V_{12}(0)\cos(\omega_L t + \tilde{\varphi}_L)(\cos\omega_L t\,\hat{\sigma}_1 + \sin\omega_L t\,\hat{\sigma}_2),$$

where $V_{12} = V_{21}$ due to the fact that the eigen functions ψ_k are real-valued.

In the rotation wave approximation (RWA) (see, for example, [14]), after averaging over oscillations of the field and transition polarization at the frequency $2\omega_L$ we get with the help of Eqs (10), (12), (13)

$$\hat{H}_L = \begin{pmatrix} 0 & \frac{1}{2}QS_{AS}e^{-i\tilde{\varphi}_L} \\ \frac{1}{2}QS_{AS}e^{i\tilde{\varphi}_L} & 0 \end{pmatrix}, \tag{14}$$

where

$$Q = k_L a_{\rm O} E_L e a_{\rm H}\sqrt{1 - \sin^2\vartheta\cos^2\varphi}\,\sin\tilde{\theta}, \tag{15}$$

$\tilde{\varphi}_L$ is the initial phase of laser field, including phase contribution, which is determined by the field polarization and molecule orientation in accordance with Eq. (10);

$$S_{AS} = \int_{-\pi}^{\pi} \psi_A(\theta)\sin\frac{\theta}{2}\,\psi_S(\theta)\,d\theta \tag{16}$$

is the dimensionless matrix element of the tunneling transition.

We can re-write the Hamiltonian (14) in the matrix form

$$\hat{H}_\Omega = \begin{pmatrix} -\frac{\hbar\delta}{2} & \frac{Q}{2}S_{AS}e^{-i\tilde{\varphi}_L} \\ \frac{Q}{2}S_{AS}e^{i\tilde{\varphi}_L} & \frac{\hbar\delta}{2} \end{pmatrix}, \tag{17}$$

where $\delta = \omega_L - \omega_{12}$ is the laser field detuning. This operator can also be expressed with the use of Pauli matrices in the form

$$\hat{H}_\Omega = \frac{\hbar}{2}\vec{\Omega}\cdot\hat{\vec{\sigma}}, \quad \vec{\Omega} = (-\delta, QS_{AS}\cos\tilde{\varphi}_L, \sin\tilde{\varphi}_L). \tag{18}$$

Time evolution operator

$$U(t) = \mathrm{T}\,\exp[(-i/\hbar)\int \hat{H}_\Omega\,dt]$$

corresponding to the operator (17) can be calculated analytically for the case of a) rectangular pulse $E_L = \text{const}$ or b) zero detuning $\delta = 0$ using the following formulae:

$$\begin{aligned} \text{a)}\quad U(t) &= \cos\left(\frac{\Omega}{2}t\right)\hat{I} - i\sin\left(\frac{\Omega}{2}t\right)\left[-\frac{\delta}{\Omega}\hat{\sigma}_3 + \frac{QS_{AS}}{\Omega}(\hat{\sigma}_1\cos\tilde{\varphi}_L + \hat{\sigma}_2\sin\tilde{\varphi}_L)\right], \\ \text{b)}\quad U(t) &= \cos\left(\frac{\Phi}{2}\right)\hat{I} - i\sin\left(\frac{\Phi}{2}\right)(\hat{\sigma}_1\cos\tilde{\varphi}_L + \hat{\sigma}_2\sin\tilde{\varphi}_L), \end{aligned} \tag{19}$$

[1]Using circular polarization gives no advantage in quadrupole approximation because polarization does not affect the dependence of the quadrupole moment of the transition on coordinate θ.

where $\Omega = \sqrt{\Omega_0^2 + \delta^2}$ is the total Rabi frequency, $\Omega_0 = QS_{AS}$ is the standard Rabi frequency, and $\Phi = \int \Omega(t)\, dt$ is the laser pulse angle.

For $\delta = 0$, we immediately find from (19b) that initial incoherent states represented as $\hat{\rho}_0 = \hat{I}/2 + w\hat{\sigma}_3/2$ ($-1 \leq w \leq 1$) transform into the states

$$\hat{\rho}_t = \frac{1}{2}\left[\hat{I} + w(\cos\Phi\,\hat{\sigma}_3 - \sin\Phi\sin(\omega_L t + \tilde{\varphi}_L)\hat{\sigma}_1 - \sin\Phi\cos(\omega_L t + \tilde{\varphi}_L)\hat{\sigma}_2)\right]. \tag{20}$$

Here, in addition to the transformation (19), free precession with the laser field frequency is also taken into account (by contrast, the latter is regularly applied in the interaction representation [15] and RWA to the operators of physical variables). In (20) the terms with $\hat{\sigma}_1$, $\hat{\sigma}_2$ represent the contribution of coherent superposition of the states ψ_S, ψ_A. In particular, for the lower initial state, which corresponds to $w = 1$ at $\omega_L t + \tilde{\varphi}_L = \pi/2$, excitation of the system by $\pi/2$-pulse, for which $\Phi = \pm\pi/2$, $\cos\Phi = \pm 1$ in (20) and $\Phi/2 = \pm\pi/4$, $\cos(\Phi/2) = \pm 1/\sqrt{2}$ in (19b), transfers the initial state ψ_S into the chiral states $\psi_{1,2} = (\psi_S \pm \psi_A)/\sqrt{2}$ corresponding to the density matrices $(\hat{I} \mp \hat{\sigma}_1)/2$. Therefore, for the fixed angles $\Theta = (\vartheta, \varphi, \tilde{\theta})$ it is possible to switch the molecule into d- or l-state with 100% probability exciting tunneling transition by a laser pulse with properly adjusted parameters. In a more general case, however, the resulting state is to be averaged over the angles Θ.

This averaging can be done with the use of standard superoperator calculation technique [16]. Performing averaging for the resulting excitation (20) of the initially incoherent state just over the sign of the parameter Q, which depends on the angle $\tilde{\theta}$ of the mean proton bonds orientation along axis X that is accounted in (20) by factor $\sin\Phi$, we receive the following structure of the density matrix:

$$\hat{\rho}_t = (\hat{I} - w\cos\Phi\hat{\sigma}_3)/2.$$

This means that in the absence of molecules orientation over angle $\tilde{\theta}$ the density matrix is transformed incoherently, i.e., diagonal matrices preserve the diagonal form. Therefore, after such kind of transformation the symmetry of each pure component S or A does not change so that the square modulus of the wave function preserves mirror symmetry with respect to the transformation $\theta \to -\theta$. As a result, we can conclude that averaging over the Θ angles cancels the effect.

How can we cope with this? An answer is that to broke the mirror symmetry the molecules should be spatially aligned during the excitation. In the section below we will examine the excitation of preliminary aligned molecules.

A. Excitation of preliminary aligned molecules

Let us assume that we were able spatially align the molecules in an ensemble. This can be done either by applying strong dc electric field (see Introduction) or by a laser pulse (sections 2, 4). If the molecules are spatially aligned, an inhomogeneity in the distribution of angle $\tilde{\theta}$ takes place and, therefore, excitation of incoherent states will contain a coherent component corresponding to the excitation of chiral states, i.e., the ones different from ψ_A and ψ_S. It is desirable to be able to characterize the effect of excitation by a simple characteristic. Let us determine the scalar property of the degree of chirality as the average value

$$\chi = 2\left(\langle\psi_l|\,\hat{\rho}\,|\psi_l\rangle - \frac{1}{2}\right) = -2\left(\langle\psi_d|\,\hat{\rho}\,|\psi_d\rangle - \frac{1}{2}\right), \tag{21}$$

where

$$\psi_{l,d} = \frac{1}{2}[\psi_S \pm \psi_A]$$

represents left and right chiral states, correspondingly, for which the corresponding degrees of chirality are $\chi = \pm 1$ for the pure states $\hat{\rho} = |\psi_{l,d}\rangle\langle\psi_{l,d}|$. For the state $\hat{\rho}(t)$ excited by a rectangular laser pulse with duration τ_p and pulse angle $\Phi = \Omega\tau_p$ the dependence of the degree of chirality on detuning δ, angle Φ, and phase $\tilde{\varphi}_L$ can be calculated analytically with the use of computer algebra.

In the simplest case, for zero laser detuning, this dependence takes the form

$$\chi = -\sin\Phi\sin\tilde{\varphi}_L.$$

For a more general case of non-zero detuning likely dependence is shown in Fig. 2a. An essential point here is that, as one can easily see from the figure, the effect depends on the laser field phase.

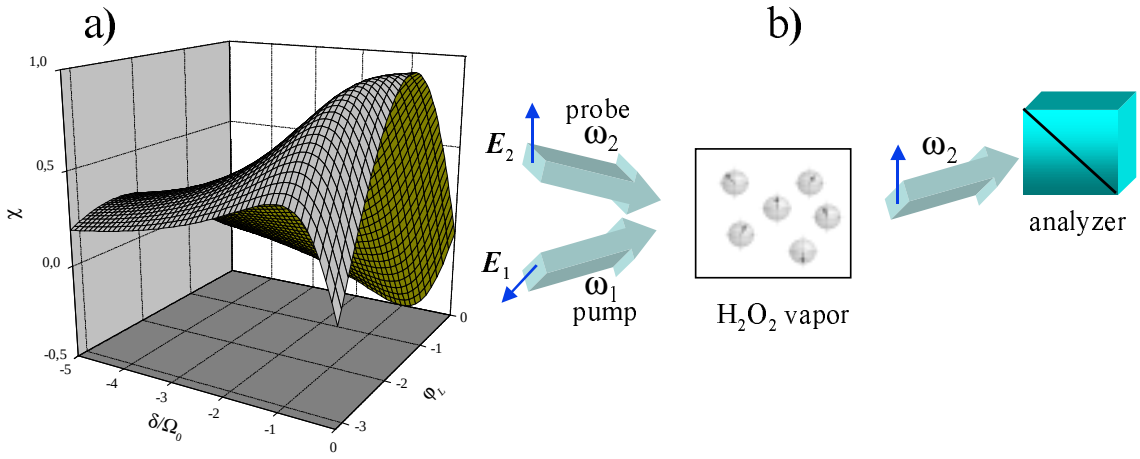

FIG. 2. a) Degree of chirality χ of the excited state vs the dimensionless detuning δ/Ω_0 and phase $\tilde{\varphi}_L$ of the incident laser field. b) An experimental setup for registration of photoinduced optical rotation in the vapor cell of H_2O_2 molecules. Two-photon Raman excitation (pump and probe laser beams) is used for driving the tunneling transition between left- and right-handed enantiomers. One of the driving system laser beams (pump) is also used for partial aligning of the molecules in the interaction region. Effect of induced optical rotation manifests itself at the probe beam frequency ω_2 and could be measured experimentally using polarization analyzer in the direction of pump beam.

IV. AN EXPERIMENTAL SCHEME FOR REGISTRATION OF PHOTOINDUCED OPTICAL ROTATION IN H_2O_2 VAPOR

In this section we discuss an experiment for registration of photoinduced optical rotation in a racemic vapor of H_2O_2 molecules.

First, we should select an effective two-level system we will work with. It seems reasonable to use for this purpose the S–A-transition of the first excited internal rotation level ($n = 1$) of the H_2O_2 torsional potential. Its wavelength and frequency are $\lambda \simeq 86$ μm and $\omega_{12} = 116.34$ cm^{-1}, respectively. The latter essentially exceeds the corresponding frequency of 11.44 cm^{-1} for the ground internal rotation level ($n = 0$).

For manipulations with the working transition we should transfer into it some population. This can be done using two-photon Raman excitation with two lasers frequency offset of which is equal to the transition frequency of the S–S-transition between ground and first excited internal rotation levels ($n = 0 \to n = 1$). As far as only dipole transitions are used in this excitation process, it seems possible to almost saturate the transition in the active volume and, therefore, for further calculations we can simply use an estimate value of $n_S \sim 1$ for the initial population value.

Due to the oscillating character of the effect, the degree of chirality will also oscillate. Therefore, it seems most consistent to use in experiment two laser fields (Fig. 2b). One of them, at the frequency ω_1, will serve as the pump field, while another one with the frequency ω_2 will be the probe, with the frequency difference $\omega_1 - \omega_2 = \omega_{12}$ in resonance with the tunneling transition. The effect of photoinduced optical rotation can be registered then with the use of two crossed polarizers, so that the registered polarization in the direction perpendicular to the probe field polarization manifests the effect of photoinduced optical rotation in a racemic vapor.

In this scheme, the probe field is used also for aligning the molecules, acting by analogy with the aligning effect in the presence of strong dc electric field that is discussed in Sec. I. In accordance with Eq. (6) the probe field affects the torsional angle, which thus oscillates with the probe field frequency ω_2. As a result, the quadrupole Hamiltonian of the interaction with the pump field with the frequency ω_1 at the frequency ω_2 and polarization vector directed along X axis receives, in accordance with Eq. (15), a contribution at the resonance frequency ω_{12}:

$$\Delta Q = \frac{E_1 E_2 e^2 a_{\rm H}^2}{8 J \omega_1^2} k_L a_{\rm O} \sqrt{1 - \sin^2\vartheta \cos^2\varphi} \times \\ \times \cos^2\tilde{\theta}\, u_1(t) u_2(t). \qquad (22)$$

At this point, an additional dependence of $\cos(\theta/2)$ on the torsional angle is to be included into the matrix element (16), which is equivalent to the substitution $\sin(\theta/2) \to (\sin\theta)/2$. The resulting matrix element is also non-zero and additional time dependence of $\cos(\omega_1 t + \varphi_1)$ corresponds to the substitution of the incident laser frequency

$\omega_L \to \omega_1 - \omega_2$ and the phase of the laser field $\tilde{\varphi}_L \to \varphi_1 - \varphi_2$. Upper bound estimation for Eq. (22) to the order of magnitude gives

$$\Delta Q \tau_p/\hbar \sim 10^{-4}\sqrt{I_1 I_2}\tau_p,$$

where laser pulses duration τ_p is given in seconds and intensities I_1, I_2 of the pump and probe laser fields are in W/cm^2. With this formula we can receive an upper estimate for the required pulse intensities, which corresponds to the action of $\pi/2$-pulse with the pulse duration of ~ 1 ns. The mean proportional intensity of the pump and probe pulses is calculated then as $I_0 = 10^4/\tau_p \sim 10^{13}$ W/cm^2.[2]

The minimum value of the measured rotation angle, $\varphi_{\min}$, and the expected value of specific rotation, $\alpha = \Delta\varphi/\Delta L$, determine the length L of the active region. A rough estimate for the α is given by $\alpha = k_L^2 a_{\rm O}(\varepsilon - 1)$, where $\varepsilon - 1 \sim 10^{-4}$ is the typical dispersion value in the visible range for H_2O_2 vapor at the normal pressure. This estimate is based on the assumption that the order of magnitude of specific rotation is characterized by additional small parameter $k_L a_{\rm O} \sim 10^{-3}$ as compared with the linear polarization response. The corresponding minimum length of the active region is $L = \varphi_{\min}/\alpha$, which is for $\varphi_{\min} = \sim 1''$ yields $L \sim 10^{-2}$ cm. It is important to note here that this characteristic interaction region length is of the same order of magnitude as the wavelength corresponding to free precession of the tunneling transition. Therefore, the propagation effects at this frequency are relatively small and can be neglected.

For the minimum value of the laser beam waist diameter $w_0^2 = \lambda_L L/\pi$ [17] in the active region the corresponding pulse power is

$$W_L = I_0 w_0^2,$$

which for the given parameters yields 10^7 W.

An experimental setup for the discussed above two-photon Raman excitation of the tunneling transition in the H_2O_2 vapor is shown in Fig. 2b. The effect of photoinduced optical rotation in the racemic vapor of equally distributed enantiomers of H_2O_2 molecule can be registered at each of the two frequencies $\omega_{1,2}$ of the pump and probe beams. Averaging over molecules orientation reveals only in the uncertainty of the Rabi frequency, due to its angle dependence $\cos^2\tilde{\theta}$. This, however, does not change the effect by order of magnitude in contrast to the method of electrostatic orientation. To avoid interference of the probe field with the frequency ω_2 with the registered at the same frequency effect in the pump field, the beams could be slightly crossed in the sample at the angle small enough not to affect the field distribution in the active region.

V. CONCLUSIONS

In conclusion, an attempt was made to answer a question: How methods of nonlinear optics can be used to induce a required sign of chirality in a racemic mixture of enantiomers of a chiral molecule? We consider a racemic mixture of left- and right-handed enantiomers of hydrogen peroxide molecule. Torsional potential of this molecule has a characteristic double-well shape minima of which correspond to the left- and right-handed enantiomers and are mirror-symmetrically spaced. As a result, a splitting of eigenstates of the torsional Hamiltonian arises from tunneling through the potential energy barrier separating the two wells. For H_2O_2 molecule this tunneling splitting is 11.4 cm-1 and 116.34 cm-1 for the internal rotation ground and first excited states, respectively, so that the the molecule shows rapid oscillations between left- and right-handed enantiomers. In a vapor or in a solution situation is complicated due to the averaging over ensemble.

Analysis of molecule-electromagnetic field interaction shows that dipole interaction does not contribute to the left-right conversion process (this interaction we can use for orientation of dipole moments of molecules in the mixture), but the quadrupole interaction, which leads to the excitation of coherent precession between left- and right-handed enantiomers' states. This gives us a tool for controlling the chiral symmetry of the molecule. We show that biharmonic Raman excitation of the splitted internal rotation levels can be effectively used for inducing optical activity in an initially racemic mixture of left- and right-handed enantiomers of H_2O_2 molecules. An experiment to study this photoinduced optical rotation in H_2O_2 vapor is proposed.

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[2]This intensity is about the intensity of the photoionization threshold for H_2O_2 molecules and therefore we should keep in experiment the intensities of the pump and probe beams on the level much less than this intensity. One can easily fit this condition by shortening the pulse duration (which cannot be made still much shorter than the internal conversion characteristic time) or by increasing the sensitivity of measuring the rotation angles. For example, for the $\pi/20$-pulses, sensitivity of about $0.01''$ and interaction length of about $L \sim 10^{-2}$ cm the required intensities are $I_0/100 \sim 10^{11}$ W/cm^2.

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